The Journal of Chemical Physics

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Cite as: J. Chem. Phys. **111**, 10275 (1999); https://doi.org/10.1063/1.480376
Submitted: 11 August 1999 . Accepted: 11 September 1999 . Published Online: 23 November 1999

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Chemical potentials and potential distributions of inclusion gas in quenched-annealed random porous media

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(Received 11 August 1999; accepted 11 September 1999)

The adsorption of hard-sphere gas in a random porous media and/or in a disordered hard sphere matrix is studied by applying the replica-Ornstein–Zernike (ROZ) equations for the quenched-annealed systems. Our interests are (1) to derive new formulas for the chemical potentials and the potential distributions theorems for such systems and (2) to use these derivations as consistency requirements for improving the closure relations in the ROZ. Two types of consistencies are enforced: (i) bulk thermodynamic property consistencies, such as the Gibbs–Duhem relation and (ii) zero-separation theorems on the cavity functions. Five hard-sphere matrix/hard-sphere fluid systems have been investigated, representing different porosities and size ratios. Direct formulas for the chemical potentials and the zero-separation theorems for the fluid cavity functions are derived and tested. We find uniformly better agreement with Monte Carlo data when self-consistency is enforced, than the conventional closures: such as the Percus–Yevick and hypernetted chain equations. In general, the structural properties are improved, as well as the thermodynamic properties. There remains discrepancy in the fluid-replica structure $h_{12}(r)$ at coincidence, $r=0$. The nature of the $h_{12}(r)$ behavior is discussed in light of the consistency principles. © *1999 American Institute of Physics.* [S0021-9606(99)70546-5]

I. INTRODUCTION

The theoretical study of inclusion gas in porous media has made a significant advance in 1988 when Madden and Glandt[1] published a paper interpreting the confining matrix and the included gas as a binary intercalation between a quenched phase (the immobile solid obstacles) and an annealed phase (the thermally equilibrated fluid). Both a cluster diagram analysis and an Ornstein–Zernike-like integral equation were presented for this quenched-annealed system. The implication is that the liquid-state theories developed in the last half century can now be brought to bear on the analyses of gas adsorption in porous media. In 1992, employing the replica method, Given and Stell[2] have reformulated this quenched-annealed (or, simply, *partly quenched or semiquenched*) system on a sound theoretical footing. The set of the Ornstein–Zernike equations derived thereby was named the replica-Ornstein–Zernike (ROZ) equations. In this formulation, the semiquenched system is taken as the limiting case of an equilibrated (annealed) mixture of $s+1$ species, where the obstacles, now mobile, are considered as one species, and the fluid plus its copies (''replicas'') are the other s species. These replicas possess a special feature: one replica species (e.g., $i=1$) does not interact across other replica species ($j=2,3,\ldots,s$). Molecules in each replica interact only within the same replica plus with the obstacle species (0). They are oblivious to the existence of other replicas. These $s+1$ species, including the obstacles, are totally equilibrated (annealed) according to standard statistical mechanics for mixtures. By taking the limit $s\to 0$ (so long as the limit exists), the quenched-annealed system of Madden–Glandt is recovered.

Since these pioneering works, a rich literature followed, employing the integral equation methods to solve for the behavior of fluids in different adsorptive systems.[3–17] The advantage of this quenched-annealed medium is that it is able to combine the factors important in adsorption such as of fluid confinement in narrow pores, the wetting of interfaces, and the disorderedness of the matrix into a single theoretical framework. Earlier numerical works starting with the ROZ were supplemented with conventional closures such as the Percus–Yevick (PY)[18] closure or the hypernetted-chain (HNC) closure[19] (*plus* some modifications), as were used in the conventional theory of bulk liquids. Some successes have been met. However, the pervasive and perverse inconsistencies inherent in these liquid-state closures were exacerbated in the semiquenched case (see, e.g., Vega *et al.*[3]) The pressure obtained from the compressibility route is different from the the grand potential. Also the free energy derived from the energy route cannot match that from the PV integration.[13] The direct consequence is that the phase diagrams determined from one route do not possess pressure consistency near the critical point.[9] It is desirable to have a theory that not only is accurate but at the same time consistent.

Previously, we have examined the issue[20] of self-consistency (abbreviated SC) for the integral equations (IE) of bulk fluids. For those cases where consistencies were enforced, the results were also highly accurate. In this work, we

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intend to extend such approaches to inclusion gas in porous media. The consistencies we shall apply can be classified into two main classes: (1) thermodynamic (or bulk) property consistencies, and (2) structural [or zero-separation theorem-(ZST)] consistencies (see, e.g., Refs. 20 and 21). These will be discussed in Secs. III and IV. As a starting point, we shall first look at a simple system: namely, hard-sphere matrices with included hard-sphere gas [denoted as HS(matrix)/HS(fluid) or simply HS/HS]. Simulation data are available for comparison.[11]

In Sec. II we write the ROZ equations together with our notational convention. In Sec. III, we shall present the thermodynamic consistencies that have applicability to these and other general potentials. Only necessary formulas appropriate for the semiquenched cases are presented. In Sec. IV, we develop new formulas for the *direct* calculation of the chemical potentials of the fluids as well as the zero-separation theorems applicable to the cavity functions. The advantage of the direct formulas is that one need not integrate over temperatures or pressures to obtain values of the chemical potentials for a given state. These direct formulas, as mentioned before,[22] depend only on correlation functions (e.g., total correlations, cavity functions, and bridge functions) at the system T and ρ. Numerical results are presented in Sec. V. We have examined five HS/HS semiquenched systems at six different state conditions representing different porosities and sphere sizes, ranging from the randomly packed matrices (penetrable spheres, $d_{00}=0$) to annealed hard-sphere matrices. In all cases, the consistency conditions have been enforced. Section VI presents the conclusion and comments of the consistency approach.

II. THE ROZ EQUATIONS

The set of ROZ equations as derived by Given and Stell[2] are given below. The label 0 indicates the matrix species; 1 the fluid species; and 2 any replica of 1. h_{ij} is the total correlation and C_{ij} is the direct correlation for the ij pair. ρ_i $(i=0,1)$ is the number density of the matrix (0) or the fluid (1) species.

$$\tilde{h}_{00}-\tilde{C}_{00}=\tilde{C}_{00}\rho_0\tilde{h}_{00}, \tag{2.1}$$

$$\tilde{h}_{01}-\tilde{C}_{01}=\tilde{C}_{01}\rho_0\tilde{h}_{00}+\tilde{C}_{11}\rho_1\tilde{h}_{01}-\tilde{C}_{12}\rho_1\tilde{h}_{01}, \tag{2.2}$$

$$\tilde{h}_{11}-\tilde{C}_{11}=\tilde{C}_{01}\rho_0\tilde{h}_{01}+\tilde{C}_{11}\rho_1\tilde{h}_{11}-\tilde{C}_{12}\rho_1\tilde{h}_{21}, \tag{2.3}$$

and

$$\tilde{h}_{12}-\tilde{C}_{12}=\tilde{C}_{01}\rho_0\tilde{h}_{01}+\tilde{C}_{11}\rho_1\tilde{h}_{12}+\tilde{C}_{12}\rho_1\tilde{h}_{11}-2\tilde{C}_{12}\rho_1\tilde{h}_{12}. \tag{2.4}$$

Note that the tilde indicates three-dimensional Fourier transform. The 12 pair is also called the blocked part, b, of the 11-correlation function, i.e., $C_{12}=C_b$. But $C_{11}=C_c+C_b$, thus $C_c=C_{11}-C_{12}$, C_c being the connected part of C_{11}. C_{11} is composed of a connected part and a blocked part (arising from diagrammatical analyses). Similar notation holds for h_c and h_b. There are four kinds of pairs, 00, 01, 11, and 12. We need also four separate closure relations to connect the total and direct correlations through the bridge functions B_{ij}. In PY, the bridge functions are given (approximately) by[18]

$$B_{ij}=\log(1+\gamma_{ij})-\gamma_{ij}, \quad i,j=0,1,2 \tag{2.5}$$

where $\gamma_{ij}=h_{ij}-C_{ij}$ is the *indirect* correlation. In this work, we shall adopt the form due to Verlet,[23] first proposed in 1980 for hard spheres, and later extensively tested by others[22,24,25]

$$B_{ij}=-\frac{\zeta_{ij}}{2}\gamma_{ij}^{*2}\left(1-\phi_{ij}+\frac{\phi_{ij}}{1+\alpha_{ij}\gamma_{ij}^{*}}\right), \quad i,j=0,1,2, \tag{2.6}$$

where α, ϕ, ζ are adjustable parameters. These are to be determined by the conditions of consistency. γ_{ij}^{*} is a *renormalized* indirect correlation function (to be specified). For the sake of imposing consistencies, we allow room for other possible types of function form. We happen to choose the Verlet form here. Our emphasis is rather on satisfying the consistency conditions than being restricted to a specific function form. The ways for determining the parameters α, ϕ, ζ are described below. These parameters turn out to be functions of the density and the sphere sizes.

III. THERMODYNAMIC CONSISTENCIES

By thermodynamic consistencies we mean the commonly known thermodynamic (Maxwell) relations on bulk properties. These should be properly modified[6,10] when applied to the semiquenched case. We identify two of these below.

A. The Gibbs–Duhem consistency

The isothermal compressibility of the fluid 1 inside the matrix is given by

$$\beta\left.\frac{\partial P_1}{\partial\rho_1}\right|_T=1-\rho_1\int d\mathbf{r}\,C_c(r), \tag{3.1}$$

where $C_c=C_{11}-C_{12}$ is the connected part of the fluid–fluid direct correlation. On the other hand, the chemical potential of the fluid 1 can be derived via the $s+1$-component mixture[26] (upon setting $s\to 0$):

$$\begin{aligned}\beta\mu_1=&\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}]\\&+\rho_1\int dr[\log y_{11}-h_{11}+(1/2)h_{11}\gamma_{11}+h_{11}B_{11}-S_{11}]\\&-\rho_2\int dr[\log y_{12}-h_{12}+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}],\end{aligned} \tag{3.2}$$

where S_{ij} are the star series (Ref. 22). The fluid must obey the Gibbs–Duhem relation [at constant temperature $dT=0$ and matrix rigidity $d\rho_0=0$ (Ref. 6)]:

$$\rho\,d\mu_1=dP_1. \tag{3.3}$$

This equation imposes a global requirement on the correlation functions. For approximate theories, the pressure obtained from (3.1) and the chemical potential from (3.2) do not satisfy (3.3). It is a sentive measure of any inconsistencies in the theory (note that PY and HNC both fail this test).

B. *dU–dP* consistency

The internal energy of the fluid 1 is given by

$$\frac{U_1}{V}=\frac{1}{2}\int d\mathbf{r}[\rho_1\rho_1 g_{11}(r)u_{11}(r)+2\rho_0\rho_1 g_{01}(r)u_{01}(r)]. \tag{3.4}$$

This energy can be integrated to give the Helmholtz free energy (i.e., via the Gibbs–Helmholtz relation), which can in turn be differentiated with respect to density to give the fluid pressure. Thus we have

$$\rho_1\frac{\partial\beta U_1}{\partial\rho_1}=\frac{\beta}{\rho_1}\frac{\partial}{\partial\beta}\left[\int d\rho_1\beta\frac{\partial P_1}{\partial\rho_1}\right]. \tag{3.5}$$

For hard spheres, there is no energy. Thus this consistency is reticent for hard core systems. We presented it here for completeness.

IV. ZERO-SEPARATION THEOREMS FOR THE CAVITY FUNCTIONS

In this section, we derive the potential distribution (i.e., zero-separation) theorems for the cavity functions y_{01}, y_{11}, and y_{12} in the semiquenched system. In the replica approach, the semiquenched system is related to a normal mixture (in the sense of equilibrium) of molecules representing the matrix and mutually noninteracting s copies (replicas) of the fluid molecules. s is an integer, but can, in the limit, approach zero. Thus the semiquenched system is recovered as the limit $(s\to 0)$ from an $s+1$-species equilibrated (annealed) mixture. We shall thus write all the formulas below in the replica system of $s+1$ species. Later, upon taking the $s\to 0$ limit, we shall converge correctly to the semiquenched system.

A. Chemical potentials

We have previously derived the direct formulas of the chemical potentials for common mixtures.[26] Application to the $s+1$ components in equilibrium gives (all chemical potentials reported below are configurational quantities, in excess of the ideal gas part):

For $\beta\mu_0$:

$$\beta\mu_0=\rho_0\int dr[\log y_{00}-h_{00}+(1/2)h_{00}\gamma_{00}+h_{00}B_{00}-S_{00}]+s\rho_1\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}]. \tag{4.1}$$

This can be abbreviated in symbolic form by using the shorthand notation

$$\rho_k\int [ij]=\rho_k\int d\mathbf{r}[\log y_{ij}-h_{ij}+(1/2)h_{ij}\gamma_{ij}+h_{ij}B_{ij}-S_{ij}]. \tag{4.2}$$

Thus (4.1) can be rewritten as

$$\beta\mu_0=\rho_0\int [00]+s\rho_1\int [01]. \tag{4.3}$$

For $\beta\mu_1$:

$$\beta\mu_1=\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}]+\rho_1\int dr[\log y_{11}-h_{11}+(1/2)h_{11}\gamma_{11}+h_{11}B_{11}-S_{11}]+(s-1)\rho_2\int dr[\log y_{12}-h_{12}+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}] \tag{4.4}$$

or

$$\beta\mu_1=\rho_0\int [01]+\rho_1\int [11]+(s-1)\rho_2\int [12]. \tag{4.5}$$

Next, in order to apply the potential distribution theorems,[21] we need to have the chemical potentials (reversible works of insertion) of *dimers* made up from pairs of species 01, 11, and 12 (a dimer is formed from two monomers when the pair interaction between the latter is annulled, as in the cavity functions). These dimers, denoted by $(1+1)$, $(1+2)$, and $(1+0)$ are at infinite dilution in the monomer fluid. Thus for the dimer $(1+1)$, formed from merging two spheres of type 1 (forcing the bond length $L\to 0$), the chemical potential is the following:

For $\beta\mu_{(1+1)}$:

$$\beta\mu_{(1+1)(L=0)}=\rho_0\int dr[\log y_{(1+1)0}-h_{(1+1)0}+(1/2)h_{(1+1)0}\gamma_{(1+1)0}+h_{(1+1)0}B_{(1+1)0}-S_{(1+1)0}]+\rho_1\int dr[\log y_{(1+1)1}-h_{(1+1)1}+(1/2)h_{(1+1)1}\gamma_{(1+1)1}+h_{(1+1)1}B_{(1+1)1}-S_{(1+1)1}]+(s-1)\rho_2\int dr[\log y_{(1+1)2}-h_{(1+1)2}+(1/2)h_{(1+1)2}\gamma_{(1+1)2}+h_{(1+1)2}B_{(1+1)2}-S_{(1+1)2}]. \tag{4.6}$$

For $\beta\mu_{(1+2)}$:

$$\beta\mu_{(1+2)(L=0)}=\rho_0\int dr[\log y_{(1+2)0}-h_{(1+2)0}+(1/2)h_{(1+2)0}\gamma_{(1+2)0}+h_{(1+2)0}B_{(1+2)0}-S_{(1+2)0}]+\rho_1\int dr[\log y_{(1+2)1}$$
$$-h_{(1+2)1}+(1/2)h_{(1+2)1}\gamma_{(1+2)1}+h_{(1+2)1}B_{(1+2)1}-S_{(1+2)1}]+\rho_2\int dr[\log y_{(1+2)2}-h_{(1+2)2}$$
$$+(1/2)h_{(1+2)2}\gamma_{(1+2)2}+h_{(1+2)2}B_{(1+2)2}-S_{(1+2)2}]+(s-2)\rho_3\int dr[\log y_{(1+2)3}-h_{(1+2)3}$$
$$+(1/2)h_{(1+2)3}\gamma_{(1+2)3}+h_{(1+2)3}B_{(1+2)3}-S_{(1+2)3}]. \tag{4.7}$$

For $\beta\mu_{(1+0)}$:

$$\beta\mu_{(1+0)(L=0)}=\rho_0\int dr[\log y_{(1+0)0}-h_{(1+0)0}+(1/2)h_{(1+0)0}\gamma_{(1+0)0}+h_{(1+0)0}B_{(1+0)0}-S_{(1+0)0}]+\rho_1\int dr[\log y_{(1+0)1}$$
$$-h_{(1+0)1}+(1/2)h_{(1+0)1}\gamma_{(1+0)1}+h_{(1+0)1}B_{(1+0)1}-S_{(1+0)1}]+(s-1)\rho_2\int dr[\log y_{(1+0)2}-h_{(1+0)2}$$
$$+(1/2)h_{(1+0)2}\gamma_{(1+0)2}+h_{(1+0)2}B_{(1+0)2}-S_{(1+0)2}]. \tag{4.8}$$

These formulas are general (for any potentials). The interaction between the composite $(1+1)$-mer, for example, with a 0-mer is *double*, in magnitude, of that between 1 and 0 mers, in the sense of site–site interactions. In the following, however, we shall specialize to the hard-sphere matrix plus hard-sphere fluid system (HS/HS) where the double of zero or infinity is still zero or infinity.

B. The coincidence values of log $y_{ij(0)}$

Next, we shall formulate the zero-separation theorems for the cavity functions. The potential distribution theorems[21] say (for HS/HS):

For $\log y_{11}(0)$:

$$\log y_{11(L=0)}=2\beta\mu_1-\beta\mu_{(1+1)(L=0)}=\beta\mu_1. \tag{4.9}$$

Since $\beta\mu_1$ is known from Eq. (4.4), we have (upon taking the $\lim_{s\to 0}$)

$$\log y_{11}(0)=\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}$$
$$-S_{01}]+\rho_1\int dr[\log y_{11}-h_{11}+(1/2)h_{11}\gamma_{11}$$
$$+h_{11}B_{11}-S_{11}]-\rho_1\int dr[\log y_{12}-h_{12}$$
$$+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}] \tag{4.10}$$

or

$$\log y_{11}(0)=\rho_0\int [01]+\rho_1\int [11]-\rho_1\int [12]=\beta\mu_1. \tag{4.11}$$

This zero-separation value is precisely the fluid chemical potential $\beta\mu_1$.

For $\log y_{12}(0)$:

$$\log y_{12(L=0)}=\beta\mu_1+\beta\mu_2-\beta\mu_{(1+2)(L=0)}$$
$$=\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}$$
$$+h_{01}B_{01}-S_{01}], \tag{4.12}$$

i.e.,

$$\log y_{12(L=0)}=\rho_0\int [01]. \tag{4.13}$$

The coincidence value of the fluid-replica pair $\log y_{12}$ depends only on the matrix-fluid correlations. This result has important implications for the fluid-replica correlation function $h_{12}(0)$, as will be discussed later.

For $\log y_{01(0)}$: The case of $\log y_{01}(0)$ is a bit more complicated. We examine three cases: Case A $d_{11}>d_{00}$; Case B $d_{11}<d_{00}$; and a nonadditive case, Case C $d_{01}>d_{00}$ and $d_{01}>d_{11}$, i.e., the 01 interaction has an effective diameter greater that both the 00 and the 11 interactions. This is the case when we have a quenched Widom–Rowlinson (QWR)-type mixture where the matrix species with diameter $d_{00}=0$ is frozen, while the fluid species (with diameter $d_{11}=0$ also) is allowed to anneal in the presence of 0. The cross interaction is with an effective diameter $d_{01}=\sigma$ that is nonzero.

Case A: $d_{11}>d_{00}$. Since

$$\log y_{01(L=0)}=\beta\mu_1+\beta\mu_0-\beta\mu_{(1+0)(L=0)} \tag{4.14}$$

for HS/HS, this becomes

$$\log y_{01}(0)=\rho_0\int dr[\log y_{00}-h_{00}+(1/2)h_{00}\gamma_{00}+h_{00}B_{00}-S_{00}]+\rho_1\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}]-\rho_1\int dr[\log y_{12}-h_{12}+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}] \quad (4.15)$$

or

$$=\rho_0\int [00]+\rho_1\int [01]-\rho_1\int [12]. \quad (4.16)$$

Note that this quantity is **not** related to the fluid chemical potential due to the [00] and [01] terms.

Case B: $d_{11}<d_{00}$

$$\log y_{01}(0)=\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}]+\rho_1\int dr[\log y_{11}-h_{11}+(1/2)h_{11}\gamma_{11}+h_{11}B_{11}-S_{11}]-\rho_1\int dr[\log y_{12}-h_{12}+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}]; \quad (4.17)$$

also,

$$=\rho_0\int [01]+\rho_1\int [11]-\rho_1\int [12]=\beta\mu_1. \quad (4.18)$$

Namely, for $d_{11}<d_{00}$, we get the fluid chemical potential.

Case C: $d_{01}>d_{00}=d_{11}$. This is the case, e.g., for the QWR,

$$\log y_{01}(0)=\rho_0\int dr[\log y_{00}-h_{00}+(1/2)h_{00}\gamma_{00}+h_{00}B_{00}-S_{00}]+\rho_1\int dr[\log y_{11}-h_{11}+(1/2)h_{11}\gamma_{11}+h_{11}B_{11}-S_{11}]-\rho_1\int dr[\log y_{12}-h_{12}+(1/2)h_{12}\gamma_{12}+h_{12}B_{12}-S_{12}]. \quad (4.19)$$

Thus

$$=\rho_0\int [00]+\rho_1\int [11]-\rho_1\int [12]. \quad (4.20)$$

For QWR, the coincidence value $\log y_{01}(0)$ is not the chemical potential $\beta\mu_1$ due to the presence of the [00] term. This fact can be further checked by comparing with the known ''exact'' values (see below). This $\log y_{01}$ of Case C is also different from Case A, because of the difference in the [01] and [11] terms.

V. NUMERICAL RESULTS

We have examined five semiquenched systems at six state conditions for HS/HS. (see Table I). Representative porosities, sphere sizes, and fluid densities are examined. (i) The first case is for diameters $d_{00}=0$, $d_{01}=\sigma$, $d_{11}=0$. This system is an analogue to the bulk Widom–Rowilinson mixture, but semiquenched, i.e., like iteractions are zero: matrix–matrix and fluid–fluid pairs do not interact. But the fluid particle and matrix particle (unlike species) interact with the hard sphere potential with diameter σ. This case, in the semiquenched mixture, is solvable exactly[4] (by the HNC closure). Thus we can use this case to check the theoretical formulas and numerical procedures. Next, (ii) $d_{00}=0$, $d_{01}=\sigma$, $d_{11}=\sigma$. In this case, the matrix particles are ideal gas particles. But they interact with the fluid particles with hard core diameter σ. Since the matrix particles themselves are penetrable, they are called a random matrix. (iii) $d_{00}=\sigma$, $d_{01}=\sigma$, $d_{11}=\sigma$. In this case, all particles (matrix and fluid) have the same range of interaction σ. The matrix is no longer random, it is an equilibrated hard sphere system, quenched into frozen obstacles. (iv) and (v) $d_{00}=3\sigma$, $d_{01}=2\sigma$, $d_{11}=\sigma$. These cases represent semiquenched systems where the matrix is composed of large spheres, three times greater than the fluid spheres. Two density states have been examined. (vi) $d_{00}=\sigma$, $d_{01}=(1/2)\sigma$, $d_{11}=0$. This case is a variation of cases (iv) and (v), only that the fluid is now ideal gas particles. Its exact thermodynamic properties are known. Thus it can again be put to good use for authentification of the theoretical and numerical procedures proposed here.

The numerical method of solution was by convolutions in bipolar coordinates.[27] The set of ROZ equations (2.1)–(2.4) consists of 11 convolutions, of which 9 are distinct. Picard's iterative solution with Broyles mixing (via a old-new solution mixing parameter) was used. Normally, 1024 grid points with grid interval 0.02σ were used. For cases (iv), (v), and (vi), 2048 grids and 4096 grids were used with size$=0.01\,\sigma$. To check convergence, the higher-grid cases did not differ much from 1024-grid cases (the difference in function values was at the 4th decimal place).

The renormalization of the indirect correlation function γ^* was achieved by adding a soft-Weeks–Chandler–Andersen (WCA) potential to the γ function[28]

$$\gamma^*(r)=\gamma(r)+(1/2)\rho f(r), \quad (5.1)$$

where $f(r)$ is the Mayer factor of the repulsive WCA 6:3 potential. The (pseudo-)temperature in this Mayer factor was set to $kT/\epsilon=9$. This number seemed to work well in the consistency process. (This is considered as another parameter that has been fitted.) The advantage of using the WCA-type potential is that it is continuous, thus avoiding discontinuities in the bridge functions when combined with the closure.

The twelve parameters: α, ϕ, and ζ (for four pairs 00, 01, 11, and 12) were determined by enforcing the consistency theorems. This number, at first glance, appears excessive. However, we have reduced the number by plausible means. First for the 00 pair (for the matrix), we have used directly α, ϕ, and ζ from Ref. 29, dedicated to the equilibrated pure hard spheres. For pairs 01, 11, and 12, we have,

TABLE I. Summary of SC calculations for the semiquenched systems: Comparison with MC (Ref. 11) and other closures.[a]

	MC	ROZ/SC (calc)	ZST and other theorems
Pair	00	01	11
Case 1	0	σ	0
	$\rho_0^*=0.1593$	$\rho_1^*=0.051\,65$	
$\beta\mu'$	0.6623 (0.667 274, exact)	0.667 407	
$\beta\partial P_1/\partial\rho_1$	0.982 (1, exact)	1.0	
Contact values			
$h_{01}(d_{10}^+)$	— (0, exact)	0	
$h_{11}(0)$	— (0.948 9179, exact)	0.949 082	
$h_{12}(0)$	— (0.948 9179, exact)	0.949 082	
Zero separation values			
$\ln y_{01}(0)$	— (0, exact)	0	
$\ln y_{11}(0)$	— (0.667 274, exact)	0.667 358	
$\ln y_{12}(0)$	— (0.667 274, exact)	0.667 358	
Parameters			
(=HNC: i.e., $\zeta=0.0$)			
Case 2:	0	σ	σ
	$\rho_0^*=0.159$	$\rho_1^*=0.381$	
$\beta\mu'$	4.168	4.11	[4.515] (4.005)
$\beta\partial P_1/\partial\rho_1$	6.40	6.28	⟨GD 6.278⟩ [5.551] (6.474)
Contact values			
$h_{01}(d_{10}^+)$	1.15	1.0	[1.187] (0.937)
$h_{11}(d_{11}^+)$	1.28	1.27	[1.555] (1.149)
$h_{12}(0)$	1.09	2.12	[1.557] (0.912)
Zero-separation values			
$\ln y_{01}(0)$		2.67	⟨⟨2.69⟩⟩ [5.090] (1.857)
$\ln y_{11}(0)$		4.17	⟨⟨4.11⟩⟩ [6.920] (2.119)
$\ln y_{12}(0)$	$\sim$0.737	1.138	⟨⟨1.125⟩⟩ [0.988] (0.648)
Parameters	α	ϕ	ζ
00	1	1.175 53	1.04834
01	1	0.956	1.0
11	1	0.999	1.0
12	1	3.297 0161	1.0
Pair	00	01	11
Case 3	σ	σ	σ
	$\rho_0^*=0.2404$	$\rho_1^*=0.383$	
$\beta\mu'$	5.97	5.815	[7.23] (5.98)
$\beta\partial P_1/\partial\rho_1$	9.003	8.149	⟨GD 8.0⟩ [7.15] (9.06)
Contact values			
$h_{01}(d_{10}^+)$	2.2603	2.186	[3.482] (2.131)
$h_{11}(d_{11}^+)$	1.6998	1.716	[2.154] (1.586)
$h_{12}(0)$	3.7975	9.240	[17.2] (2.965)
Zero-separation values:			
$\ln y_{01(0)}$		5.822	⟨⟨5.815⟩⟩ [13.6] (2.807)
$\ln y_{11}(0)$		5.819	⟨⟨5.815⟩⟩ [12.4] (2.706)
$\ln y_{12}(0)$	1.590	2.326	⟨⟨2.327⟩⟩ [2.89] (1.377)
Parameters	α	ϕ	ζ
00	1	1.175 53	1.048 34
01	1	0.986 382 25	1.0
11	1	0.986 118 03	1.0
12	1	1.316 0243	1.0
Case 4	3σ	2σ	σ
	$\rho_0^*=0.0179$	$\rho_1^*=0.4811$	
$\beta\mu'$	9.754	8.674	[9.493] (8.637)
$\beta\partial P_1/\partial\rho_1$	8.66	15.72	⟨GD 16.5⟩ [11.77] (13.07)
Contact values			
$h_{01}(d_{10}^+)$	6.842	6.501	[8.929] (3.351)
$h_{11}(d_{11}^+)$	3.681	3.778	[4.83] (1.798)
$h_{12}(0)$	4.208	12.93	[23.0] (1.780)
Zero-separation values			
$\ln y_{01}(0)$		8.687	⟨⟨8.674⟩⟩ [17.37] (2.939)
$\ln y_{11}(0)$		8.6705	⟨⟨8.674⟩⟩ [23.63] (2.963)
$\ln y_{12}(0)$	$\sim$1.65	2.635	⟨⟨2.6435⟩⟩ [3.177] (1.023)
Parameters	α	ϕ	ζ
00	1	0.998 092	1.018 157

TABLE I. (*Continued.*)

	MC	ROZ/SC (calc)	ZST and other theorems
01	1	0.986 698 02	1.0
11	1	0.984 532 43	1.0
12	1	1.280 7651	1.0
	00	01	11
Case 5	3σ	2σ	σ
	$\rho_0^*=0.0179$	$\rho_1^*=0.369$	
$\beta\mu'$	5.902	5.46	
$\beta\partial P_1/\partial\rho_1$	10.42	8.75	⟨GD 8.786⟩
Contact values			
$h_{01}(d_{10}^+)$	4.336	4.039	
$h_{11}(d_{11}^+)$	2.447	2.473	
$h_{12}(0)$	2.295	5.789	
Zero-separation values			
$\ln y_{01}(0)$		5.47	⟨⟨5.46⟩⟩
$\ln y_{11}(0)$		5.47	⟨⟨5.46⟩⟩
$\ln y_{12}(0)$	1.192	1.917	⟨⟨1.910⟩⟩
Parameters	α	ϕ	ζ
00	1	0.998 092	1.018157
01	1	0.980 512 72	1.0
11	1	0.976 392 96	1.0
12	1	1.519 164	1.0
Case 6	σ	$1/2\sigma$	0
	$\rho_0^*=0.30$	$\rho_1^*=0.30$	
$\beta\mu'$	0.170 97 (0.170 88, exact)	0.1713	[1.714]
$\beta\partial P_1/\partial\rho_1$	0.992 06	1.000 013	⟨GD 1.0⟩[1.0]
Contact values			
$h_{01}(d_{10}^+)$	0.188	0.189	[0.198]
$h_{11}(0)$		0.187	[0.186]
$h_{12}(0)$	0.158	0.188	[0.186]
Zero-separation values			
$\ln y_{01}(0)$		0.1855	⟨⟨0.1713⟩⟩ [0.1782]
$\ln y_{11}(0)$		0.1718	⟨⟨0.1713⟩⟩ [0.1865]
$\ln y_{12}(0)$	0.147	0.172 65	⟨⟨0.1713⟩⟩ [0.1865]
Parameters	α	ϕ	ζ
00	1	1.0745	1.0352
01	1	0.809 1418	1.0
11	1	0.984 5324	1.0
12	1	1.280 7651	1.0

[a]⟨GD:⋯⟩=Gibbs–Duhem; ⟨⟨⋯⟩⟩=zero-separation results; [⋯]=HNC; (⋯)=PY; ROZ=Replica-OZ equations; SC=self-consistency closure results.

for the sake of simplicity of fitting, set α, and ζ's to unity ($=1$). Thus only three parameters ϕ's (for 01, 11, 12) are left to vary, in such a way that the ZST's in Sec. IV B be satisfied. By actually carrying out this fitting, we found, as *fait accompli*, that the thermodynamic consistencies in Sec. III A (i.e., the Gibbs–Duhem relation) were well satisfied.

Case (i): The quenched Widom–Rowlinson mixture

For this case, $d_{00}=0$, $d_{01}=\sigma$, $d_{11}=0$ at $\rho_0\sigma^3=0.1593$, $\rho_1\sigma^3=0.051\,63$. This QWR possesses results which are exactly given by the HNC solution.[4] The following facts are observed: (a) The 00 matrix part is an ideal gas. Thus $h_{00}(r)=0=C_{00}(r)$. (b) The 01 matrix-fluid part gives $h_{01}(r)=f_{01}(r)=C_{01}(r)$, where f_{01} is the Mayer factor for the 01 interaction. Also, $y_{01}(r)=1$, $B_{01}(r)=0$. (c) The 11 fluid–fluid part has $h_{11}(r)-C_{11}(r)=\rho_0 f_{10}{*}f_{01}$, where asterisk indicates convolution. $B_{11}(r)=0$, $h_{11}(r)=h_{12}(r)$, $C_{11}(r)=C_{12}(r)$, $y_{11}(r)=y_{12}(r)$. We summarize the exactly known correlation functions below:

$$h_{00}(r)=0, \tag{5.2}$$

$$h_{01}(r)=f_{01}(r), \tag{5.3}$$

$$h_{11}(r)=h_{12}(r)=\exp(\rho_0\Omega_0(r))-1, \tag{5.4}$$

where $\Omega_0(r)$ is the overlap volume of two spheres at a distance r apart, i.e., the convolution of the Mayer factors $f_{10}{*}f_{01}$:

$$C_{00}(r)=0, \tag{5.5}$$

$$C_{01}(r)=f_{01}(r), \tag{5.6}$$

$$C_{11}(r)=C_{12}(r)=\exp(\rho_0\Omega_0(r))-1-\rho_0\Omega_0(r). \tag{5.7}$$

Thus (within HNC, where $B=0$)

$$\log y_{00}(r)=0, \tag{5.8}$$

$$\log y_{01}(r)=0, \tag{5.9}$$

$$\log y_{11}(r)=\log y_{12}(r)=\rho_0\Omega_0(r). \tag{5.10}$$

The consequence on the chemical potential $\beta\mu_1$ is

$$\begin{aligned}\beta\mu_1=&\rho_0\int d\mathbf{r}[\underline{\log y_{01}}-h_{01}+(1/2)h_{01}\underline{\gamma_{01}}+h_{01}\underline{B_{01}-S_{01}}]\\&+\rho_1\int d\mathbf{r}[\underline{\log y_{11}}-\underline{h_{11}}+(1/2)\underline{h_{11}\gamma_{11}}+h_{11}\underline{B_{11}-S_{11}}]\\&-\rho_2\int d\mathbf{r}[\underline{\log y_{12}}-\underline{h_{12}}+(1/2)\underline{h_{12}\gamma_{12}}+h_{12}\underline{B_{12}-S_{12}}]\\=&\rho_0\int d\mathbf{r}[-h_{01}]\\=&\rho_0\int d\mathbf{r}[-f_{01}]\\=&\rho_0\int_0^\sigma dr\,4\pi r^2=\frac{4\pi}{3}\rho_0\sigma^3=0.667\,274\ \ (\text{exact}),\end{aligned} \tag{5.11}$$

where the underlined quantities are zero, while underbraced quantities cancel each other. The outputs from numerically solving the ROZ (with the HNC closure) are compared with the analytical results in Table I. This case can be used to check (1) the validity of the theoretical formulas (the expressions for the chemical potentials and zero-separation theorems as given earlier); and (2) the accuracy of the numerical procedures utilized. For example, the numerical value of $\beta\mu_1$ obtained by solving the ROZ equation and then substituting the correlation functions into the direct formula Eq. (4.4) was 0.667 407 (cf. exact 0.667 274). This indicates that both the direct formulas we derived and the numerical procedures employed were justified. (Of course, one case does not constitute a proof. It is a check. The proof is in the replica-based derivations, Sec. IV B.) Note that the MC value from Ref. 11 is 0.6623. Next, the coincidence value of $\log y_{12}(0)$ should be

$$\begin{aligned}\log y_{12(L=0)}=&\rho_0\int dr[\underline{\log y_{01}}-h_{01}+(1/2)h_{01}\underline{\gamma_{01}}\\&+h_{01}\underline{B_{01}-S_{01}}]\\=&\rho_0\int dr[-h_{01}]=\frac{4\pi}{3}\rho_0\sigma^3\\=&0.667\,274\ \ (\text{exact}).\end{aligned} \tag{5.12}$$

From numerical solution of the ROZ, the value of $\log y_{12}(0)$ at $r=0$ was found to be 0.667 358. Thus the numerical procedure is accurate to the third decimal place. Similarly, the value of $\log y_{11}(0)$ will be found from

$$\begin{aligned}\log y_{11}(0)=&\rho_0\int dr[\underline{\log y_{01}}-h_{01}+(1/2)h_{01}\underline{\gamma_{01}}\\&+h_{01}\underline{B_{01}-S_{01}}]+\rho_1\int dr[\underline{\log y_{11}}-\underline{h_{11}}\\&+(1/2)\underline{h_{11}\gamma_{11}}+h_{11}\underline{B_{11}-S_{11}}]-\rho_1\int dr[\underline{\log y_{12}}\\&-\underline{h_{12}}+(1/2)\underline{h_{12}\gamma_{12}}+h_{12}\underline{B_{12}-S_{12}}]\\=&\rho_0\int dr[-h_{01}]=\frac{4\pi}{3}\rho_0\sigma^3=0.667\,274\ \ (\text{exact}).\end{aligned} \tag{5.13}$$

Direct calculation gave 0.667 358.

For $\log y_{01}(0)=0$, the formula is (Case C)

$$\begin{aligned}&\log y_{01}(0)\\&=\rho_0\int dr[\underline{\log y_{00}}-\underline{h_{00}}+(1/2)\underline{h_{00}\gamma_{00}+h_{00}B_{00}-S_{00}}]\\&+\rho_1\int dr[\underline{\log y_{11}}-\underline{h_{11}}+(1/2)\underline{h_{11}\gamma_{11}}\\&+h_{11}\underline{B_{11}-S_{11}}]-\rho_1\int dr[\underline{\log y_{12}}-\underline{h_{12}}\\&+(1/2)\underline{h_{12}\gamma_{12}}+h_{12}\underline{B_{12}-S_{12}}]=0.\end{aligned} \tag{5.14}$$

Numerically, we also obtained zero value, as the formula says. The isothermal compressibility for the fluid from numerical calculation [via Eq. (3.1)] is the exact value 1.0 [because $C_c(r)=0$]. The three facts (a), (b), and (c) listed above for the correlation functions were all reproduced in our numerical procedures.

Case (ii): $d_{00}=0$, $d_{01}=\sigma$, $d_{11}=\sigma$

At $\rho_0\sigma^3=0.159$, $\rho_1\sigma^3=0.381$, the numerical results for this random matrix mixture are given in Table I. The chemical potential of the fluid was calculated to be $\beta\mu_1=4.11$. The MC value of Meroni *et al.* is 4.168. The zero-separation value $\log y_{11}(0)$ was obtained as 4.17. This value had been forced to agree with $\beta\mu_1=4.11$ according to the zero-separation theorem (e.g., by varying ϕ_{11}). The contact values of $h_{11}(\sigma)$ and $h_{01}(\sigma)$ (1.27 and 1.0, respectively) are also close to MC simulations (1.28 and 1.15). The values from HNC and PY are also listed for comparison. They are (HNC: 1.555 and 1.187, respectively), and (PY: 1.149 and 0.937, respectively). The isothermal compressibility calculated is 6.28 vs MC 6.40. Note that we have also enforced the Gibbs–Duhem relation, Eq. (3.3). The derivative of the chemical potentials yields an isothermal compressibility of 6.278 (GD). Direct computation with Eq. (3.1) gives 6.28.

The correlation functions: h_{ij}, $\log y_{ij}$, and B_{ij} are displayed in Figs. 1 and 2. The total correlations h_{01} and h_{11} are in good agreement with MC data from Ref. 11. The fluid-

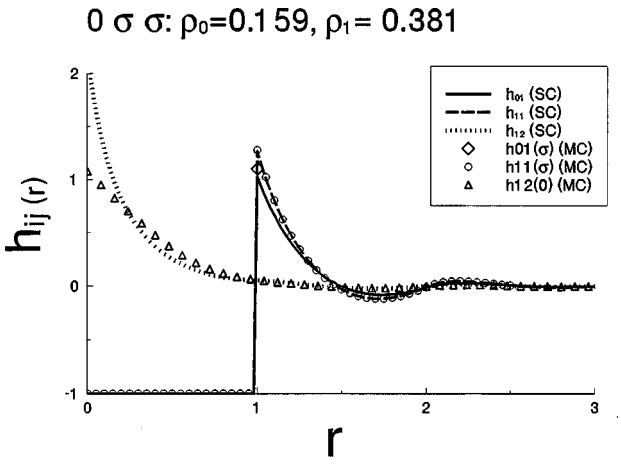

FIG. 1. Case 2: Total correction functions h_{01}, h_{11}, and h_{12} at $\rho_0=0.159$ and $\rho=0.381$. Matrix sphere has size 0, $d_{00}=0$ (i.e., random matrix), fluid-matrix $d_{01}=\sigma$, fluid–fluid $d_{11}=\sigma$. Symbols=MC (Ref. 11). Lines=SC (self-consistent) calculations as presented here. (Solid line and diamond=01 pair. Dashed line and circles=11 pair. Dotted line and triangles=12 pair.) Note the close agreement for $h_{11}(r)$ between MC (circles) and SC (dashes) results. The $h_{12}(r)$ is an agreement at $r>0.8$. At coincidence, there are visible differences (see text for discussions).

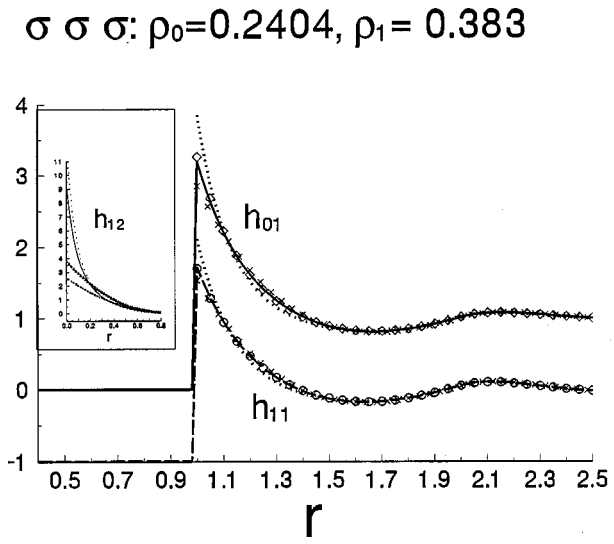

FIG. 3. Case 3: Total correction functions h_{01}, h_{11}, and h_{12} at $\rho_0=0.2404$ and $\rho_1=0.383$. Matrix sphere has size $d_{00}=\sigma$, fluid-matrix $d_{01}=\sigma$, fluid–fluid $d_{11}=\sigma$. Symbols: diamonds, circles, and triangles=MC (Ref. 11). The SC is compared with HNC and PY closures. Solid and dashed lines=SC. Dotted line=HNC. Crosses=PY. It is seen that the HNC and PY values bracket the MC and SC curves. The agreement of SC with MC for h_{01} and h_{11} is very close. For h_{12}, there is discrepancy at coincidence ($r=0$). HNC and PY are less satisfactory compared to SC as theories for this semiquenched system.

replica h_{12} at coincidence is overpredicted by the SC closure (Fig. 1). The SC $\log y_{ij}$ were forced to satisfy the zero-separation theorems (according to our consistency requirements) by varying the parameters α, ϕ, ζ until agreement is achieved. It is seen that 01 and 11 pairs (2.67 and 4.17) conform to the ZSEP required values (=2.69, 4.11), respectively. The MC value of $\log y_{12}(0)$ is 0.73, while our prediction is 1.14 (in conformity with the ZSEP requirement =1.13). This overprediction of the coincidence value $\log y_{12}(0)$, as compared with MC, is a recurring feature of our SC approach for all cases studied (except for QWR). Checking the PY and HNC results shows that the SC value (1.14) is closer to the HNC value (0.938) than the PY value (0.648). The bridge functions are presented in Fig. 2. The coincidence value $B_{12}(0)=0.232$ is slightly greater than 0. This function is small in magnitude.

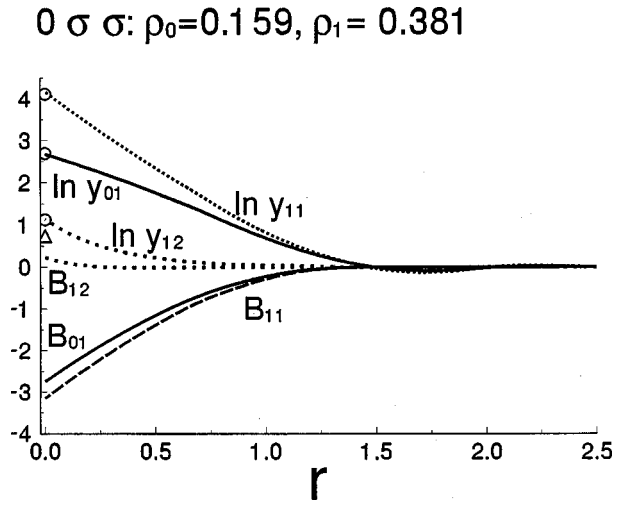

FIG. 2. Case 2: Cavity and bridge functions: $\ln y_{01}$, $\ln y_{11}$, $\ln y_{12}$, B_{01}, B_{11}, and B_{12}. (For legend, see Fig. 1.) Open circles are the coincidence values of $\ln y_{ij}(0)$ according to the ZST (zero-separation) theorems [i.e., Eqs. (4.10); (4.12); (4.16) for this case]. That the lines go through these points indicates the fulfillment of structural consistency (see text). The MC (triangle) value $\ln y_{12}(0)$ is lower then the ZST circle, indicating some uncertainties (see Sec. VI).

Case (iii): $d_{00}=\sigma$, $d_{01}=\sigma$, $d_{11}=\sigma$

This case is at $\rho_0\sigma^3=0.2404$, $\rho_1\sigma^3=0.383$. All diameters have the same size σ. The fluid particles are of comparable dimension as the hard-sphere matrix. The results are presented in Table I. The calculated chemical potential is 5.815 (vs MC 5.97). Isothermal compressibility 8.149 (vs MC 9.0). The zero separation values $\log y_{11}(0)$ calculated =5.822 (which according to ZST should be $\beta\mu_1=5.815$). Thus ZST is closely satisfied. Similarly, $\log y_{01}(0)=5.819$ (which according to ZST should be $\beta\mu_1=5.815$).

On the other hand, $\log y_{12}(0)$ calculated is 2.326 (vs MC=1.590 and ZST demands 2.327). The basic difference derives from the incongruities between the MC value and the value required by the zero-separation theorems. How do we account for this difference? Let us consider the ZST Eq. (4.12) for $\log y_{12}(0)$. It depends on the matrix-fluid 01 correlations *only*. Thus, in principle, no matter how one gets $y_{12}(0)$ (be it from MC or from some other sources), this $y_{12}(0)$ must satisfy the ZST (derived from the principle of potential distribution theorem, a well-defined physicochemical principle). Namely, its value should be consistent with the matrix-fluid 01 correlations. Let us examine how good the SC 01 correlations are. One indication is that Fig. 3 shows that the $h_{01}(r)$ from SC is well in agreement with MC. Thus using either SC or MC correlations, one should get, via Eq. (4.12), similar $\log y_{12}(0)$. This is not the case. Our (SC) results gave $\log y_{12}(0)=2.327$ (not 1.590 from

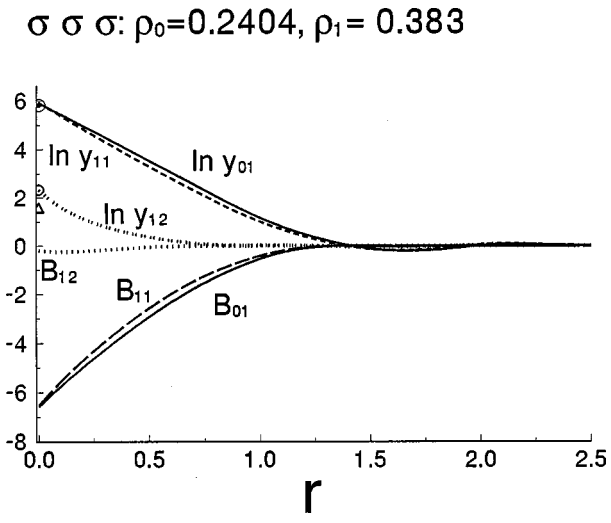

FIG. 4. Case 3: Cavity and bridge functions: $\ln y_{01}$, $\ln y_{11}$, $\ln y_{12}$, B_{01}, B_{11}, and B_{12}. (For legend, see Fig. 3.) Open circles are the coincidence values of $\ln y_{ij}(0)$ according to the ZST theorems [Eqs. (4.10); (4.12); (4.18)]. That the lines go through these points indicates the fulfillment of structural consistency (see text). The MC (triangle) value $\ln y_{12}(0)$ is a bit low.

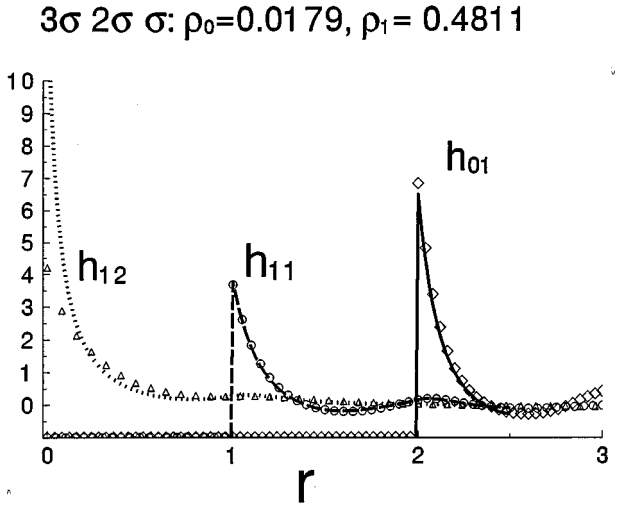

FIG. 5. Case 4: Total correction functions h_{01}, h_{11}, and h_{12} at $\rho_0=0.0179$ and $\rho_1=0.4811$. Matrix sphere has size $d_{00}=3\sigma$, fluid-matrix $d_{01}=2\sigma$. fluid–fluid $d_{11}=\sigma$. Symbols: diamonds, circles, and tringles=MC (Ref. 11). Solid, dashed, and dotted lines=SC. It is seen that the agreement of SC with MC for h_{01} and h_{11} functions are reasonable. For h_{12}, there is discrepancy at coincidence ($r=0$). For $r>0.8$, the agreement regains validity. Note that the packing fraction is around $\eta\sim 0.505$, a densely packed case. In light of high density, the accord between SC and MC is remarkable.

MC). If we trust the SC 01 correlations (already verified independently by MC), then this coincidence value (2.327) should be *correct*. In other words, the MC values for 01 correlations should have been consistent, via the ZST (4.12), with the MC $\log y_{12}(0)$, and this is not so (with MC 1.590 vs ZST 2.327). We note that the discrepancy is confined only near coincidence $r\to 0$. For larger $r(>0.6)$, the agreement of SC with MC is good.

The correlation functions: h_{ij}, $\log y_{ij}$, and B_{ij} are displayed in Figs. 3 and 4. The $h_{01}(r)$ from SC compares well with MC, as remarked. To put things in perspective, we also included the HNC and PY results. HNC tends to overpredict, while PY under-predict the MC values. The cavity functions as shown (Fig. 4) obey the ZST (as a consequence of the consistency requirements). The bridge functions appear in Fig. 4. The 12-pair again has small values.

Cases (iv) and (v): $d_{00}=3\sigma$, $d_{01}=2\sigma$, $d_{11}=\sigma$

Two fluid densities are investigated: $\rho_1\sigma^3=0.369$ and $=0.4811$. (The matrix porosity is $\rho_0\sigma^3=0.0179$.) The matrix particle size is three times greater than that for the fluid particles (or 9 times greater in volume). The results are presented in Table I. For the high fluid density case, the calculated chemical potential is 8.674 (vs MC 9.75). Isothermal compressibility 15.72 (vs MC 8.66). The GD isothermal compressibility is for this case=16.5. We recall that these two cases in the original simulation work[11] involved exceptionally small number of matrix realizations ($NQ=8$ and 10, instead of $NQ=40$ for the other cases). The MC statistics were consequently poorer. For the low fluid density case, the calculated SC chemical potential is 5.46 (vs MC 5.902). The SC isothermal compressibility 8.75 (vs MC 10.4). The GD isothermal compressibility is for this case=8.79. We consider these numbers to be in fair agreement.

The SC values for the high fluid density case are $\log y_{01}(0)=8.687$, and $\log y_{11}(0)=8.671$ (which according to ZST should be $\beta\mu_1=8.674$). The contact values of $h_{11}(\sigma)$ and $h_{01}(\sigma)$ (3.778 and 6.50) are reasonably close to MC simulations (3.68 and 6.84). However, the fluid-replica pair exhibits the same discrepancy as in Case (iii). $\log y_{12}(0)=2.635$ (vs MC 1.65, ZST 2.643, HNC 3.177, and PY 1.78).

The correlation functions at $\rho_1=0.4811$ are presented in Figs. 5 and 6. The cavity $\log y_{10}(r)$ shows a region of con-

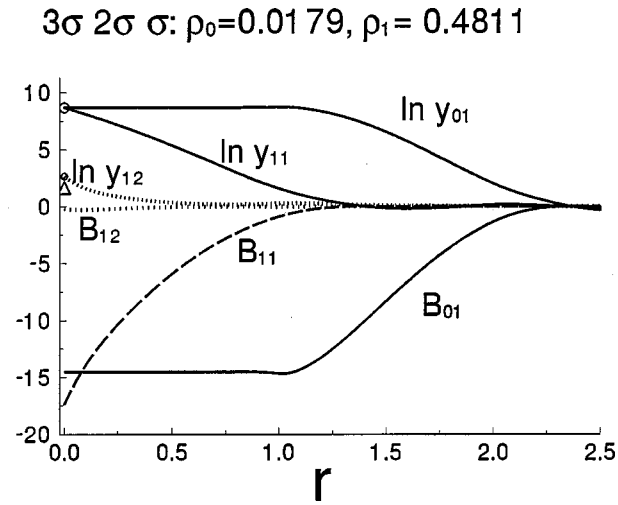

FIG. 6. Case 4: Cavity and bridge functions: $\ln y_{01}$, $\ln y_{11}$, $\ln y_{12}$, B_{01}, B_{11}, and B_{12}. (For legend, see Fig. 5.) Open circles are the ZST coincidence value for $\ln y_{ij}(0)$ [Eqs. (4.10); (4.12); (4.18)]. We have achived ZST consistency. The MC (triangle) value is lower then SC, as has been seen in several case studies already. The value of $\ln y_{01}(r)$ is constant inside the matrix sphere (since $d_{00}=3\sigma$), similar to the bulk hard sphere mixture case.

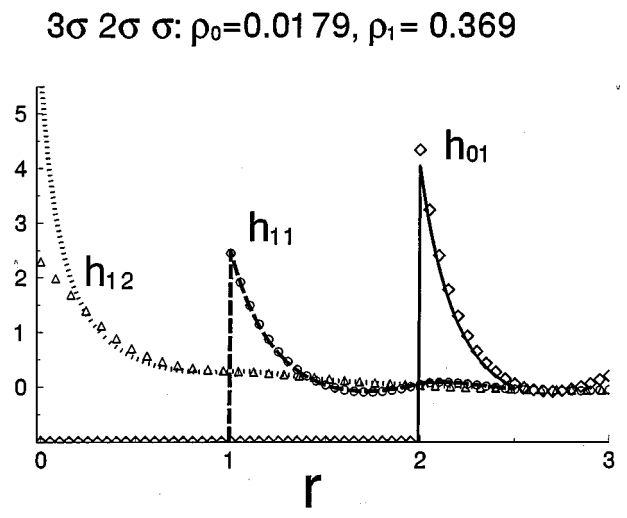

FIG. 7. Case 5: Total correction functions h_{01}, h_{11}, and h_{12} at $\rho_0=0.0179$ and $\rho_1=0.369$, the lower fluid density case. Matrix sphere has size $d_{00}=3\sigma$, fluid-matrix $d_{01}=2\sigma$, fluid–fluid $d_{11}=\sigma$. (Legend same as Fig. 5.) The agreement for the SC and MC h_{01} and h_{11} functions is satisfactory. For h_{12}, deviations are manifest near $r=0$. However, for $r>0.8$, the agreement recovers.

stant value ($r<\sigma$). This is due to the large size of the matrix sphere ($d_{00}=3\sigma$) that occluded the fluid sphere ($d_{00}=\sigma$) for $r<\sigma$, similar to the bulk binary hard sphere mixture with same size ratios. For $\rho_1=0.369$, Figs. 7 and 8 give the total, cavity, and bridge functions. Comparison with MC data shows that h_{01} and h_{11} from SC are fiduciary.

Case (vi): $d_{00}=\sigma$, $d_{01}=(1/2)\sigma$, $d_{11}=0$

Note that $\rho_0=\rho_1=0.30$. This case is similar to the previous case, except that the fluid now is composed of ideal gas particles. The reason for studying this case is that a number of its thermodynamic properties are known exactly. Thus, it can be used to check the validity of the numerical procedures (and indirectly the theoretical formulas). For example, the excess chemical potential is given exactly by

$$\beta\mu_1=-\log\left(1-\frac{\pi}{6}\rho_0\sigma_0^3\right)=0.170\,88 \quad \text{(exact)}. \tag{5.15}$$

From SC calculations (Table I), we get $\beta\mu_1=0.1713$ ($+0.2\%$). From ZST, we infer that $\log y_{01}(0)$ and $\log y_{11}(0)$ should also be $\beta\mu_1=0.1713$. SC calculated $\log y_{01}(0)=0.185$ (vs HNC 0.178) and $\log y_{11}(0)=0.1718$ (vs HNC 0.1865). ZST gives $\log y_{12}(0)=0.1713$, while SC-calculated $\log y_{12}(0)=0.1727$ (vs MC=0.147, lower than the SC value of 0.1727). For $h_{10}(d_{10})$, SC=0.189, while MC=0.188 (HNC 0.198). The MC value for $h_{12}(0)=0.158$ is smaller than the SC value=0.1885. This under-estimation by MC is also evident from the original paper [in their Fig. 10 (Ref. 11)]. The correlation functions from SC gave $h_{11}=h_{12}$. As a consequence, the isothermal compressibility is 1 [because $h_c(r)=0$]. This is also a known (exact) result.

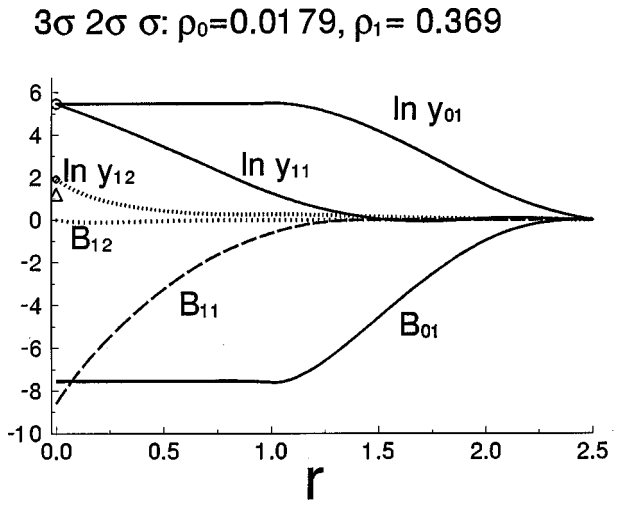

FIG. 8. Case 5: Cavity and bridge functions: $\ln y_{01}$, $\ln y_{11}$, $\ln y_{12}$, B_{01}, B_{11}, and B_{12}. (For legend, see Fig. 7.) Open circles are the ZST coincidence value for $\ln y_{ij}(0)$ [Eqs. (4.10); (4.12); (4.18)]. For $\ln y_{12}(0)$, MC (triangle) value differs a bit from the SC curve.

VI. CONCLUSIONS

In this paper, we have derived the formulas for the chemical potentials and the zero-separation theorems for the cavity functions of fluids confined in a porous matrix. These formulas can be utilized to aid the construction of closure relations. We call this approach the self-consistency approach. In practice, we have adopted a closure form from Verlet, that is made ''flexible'' with several inherent parameters. These SC closures were tested on the HS(matrix)/HS(fluid) and random matrix/HS(fluid) systems within the replica-Ornstein–Zernike formalism. Five matrix systems (with six state conditions) were examined. The structural and thermodynamic results are found to be accurate in comparison with Monte Carlo results. The SC performs better than the usual liquid closures: e.g., Percus–Yevick or hypernetted chain equations. On the other hand, there is disagreement between SC and MC regarding the fluid-replica correlation h_{12}, especially at $r=0$ (coincidence value). As a superficial observation: the HNC and PY values usually bracket the MC results. Our results (SC) are closer to the HNC, while the PY results are closer to the MC. For example, for Case 3, the ordering of $h_{12}(0)$ is HNC (17.1)>SC (9.24)>MC (3.79)>PY (2.96). For Case 4, HNC (23.0)>SC (12.93)>MC (4.21)>PY (1.78). There is quite a range of variation for this value. To find the origin of the difference, we propose the following analysis [we have alluded to this reasoning earlier in the discussions for Case (iii)].

The zero-separation theorem on $\log y_{12}(0)$ has been shown [in Eq. (4.12)]

$$\log y_{12(L=0)}=\rho_0\int dr[\log y_{01}-h_{01}+(1/2)h_{01}\gamma_{01}+h_{01}B_{01}-S_{01}] \tag{6.1}$$

to depend only on the matrix-fluid (01) correlations. Thus here we have a consistency check: that the value $h_{12}(0)=y_{12}(0)-1$ should be related through Eq. (6.1) to the 01 correlation functions and the 01 correlations only. In other word, if the 01 correlations are correctly calculated (from MC, SC or other sources), one can obtain the coincidence

value of $h_{12}(0)$ through (6.1). This constitutes a consistency requirement. The existing facts are (i) in Case 3 for example, the $h_{01}(r)$ obtained from SC checks with MC results for the entire range of r (see Fig. 5). It suggests that the SC data for 01 are accurate. (ii) From Eq. (6.1), using the SC 01 correlations only, we obtained ZST $\log y_{12}(0)=2.327$. Next, from direct ROZ numerical calculations, we obtained SC $\log y_{12}(0)=2.326$ [this was made to conform to Eq. (6.1), the ZST]. This means that the SC solution has been made successfully consistent with respect to the ZST (6.1). On the other hand, the MC $\log y_{12}(0)=1.590$ (<2.327). This means that the simulated total correlation function MC $h_{12}(r=0)$ at coincidence is not ZST consistent with the MC simuated 01 correlations. In the original paper,[11] the difficulties of simulating the replica (12) correlation functions, especially near $r=0$, have been carefully examined. Thus we draw the conclusion that our SC results of the 12 structures (i) to be at least ZST-consistent (definitely better than the HNC or PY results). (ii) The accuracy of SC results regarding $h_{12}(0)$ will have to be reconfirmed by new simulation data or other independent means of authentification. Our discussions above concern only the point at coincidence $r=0$. For larger r, the agreement of SC and MS is again good.

In sum, we have presented here (1) new formulas for the chemical potentials and zero-separation theorems; and (2) self-consistent ROZ closures that also give highly accurate results. The disordered media we have considered are relatively simple, at this initial stage of study (namely, hard sphere matrix+hard sphere fluid). We envision, for future investigation, studies of industrially more interesting materials with attractive affinities, so that the wetting behavior, phase transitions,[30,31] as well as compliant structures can be examined. The methodology developed here can aid in these endeavors.

ACKNOWLEDGMENTS

We acknowledge the Spanish Dirección General de Enseñanza Superior e Investigación Científica for partial support of this project under Grant No. PB97-0258-C02-02 and the sabbatical leave for L.L.L. (Grant No. SAB95-0646.) Dr. Jean-Jacques Weis and Dominique Levesque have kindly provided the original Monte Carlo data for comparison and given insights into the problem, for which we are grateful.

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